

Unclassified

DTIC
ELECTE
JAN 04 1990

14 DEC 1989

②

AD-A216 320

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS EC		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			4. PERFORMING ORGANIZATION REPORT NUMBER(S)		
5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR. 89-1818			6a. NAME OF PERFORMING ORGANIZATION Columbia University		
6b. OFFICE SYMBOL (If applicable)			7a. NAME OF MONITORING ORGANIZATION Air Force Office of Scientific Research		
6c. ADDRESS (City, State and ZIP Code) New York, New York 10027			7b. ADDRESS (City, State and ZIP Code) Bolling Air Force Base, Bldg. 410 Bolling Air Force Base, D.C. 20332		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Air Force Office of Sci. Res. NC			8b. OFFICE SYMBOL (If applicable)		
8c. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling Air Force Base, D.C. 20332			9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-88-0043		
11. TITLE (Include Security Classification) FINAL REPORT (Unclassified) Dynamics and Stabilization of Materials Possessing High Energy Content			10. SOURCE OF FUNDING NOS.		
12. PERSONAL AUTHOR(S) Nicholas J. Turro			10. SOURCE OF FUNDING NOS.		
13a. TYPE OF REPORT final			13b. TIME COVERED FROM 1987 TO 89		
13c. DATE OF REPORT (Yr., Mo., Day) November 13, 1989			15. PAGE COUNT 12		
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	porous solids; silica; biradicals; polymers;		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The accomplished research has involved (1) the construction of new instrumentation for the investigation of transient high energy materials; (2) the exploration of how the chemistry of transient high energy materials is modified by adsorption on the surfaces at interfaces; and (3) the exploration of how the chemistry and dynamics of high energy density materials respond to systematic variations in structure, and experimental variables such as pressure, magnetic fields and temperature. Particular emphasis has been given to reactions in microheterogeneous environments and interfaces provided by micelles, polymers and porous solids. Since the initiation of this grant, a time resolved electron spin resonance spectrometer and a time resolved NMR spectrometer capable of measuring CIDNP spectra on a routine basis have been constructed.</p>					
90 01 04 125					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input checked="" type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg			22b. TELEPHONE NUMBER (Include Area Code) (202) 767-4963		22c. OFFICE SYMBOL AFOSR/NC

14 DEC 1989

DYNAMICS AND STABILIZATION OF MATERIALS
POSSESSING HIGH ENERGY CONTENT

Nicholas J. Turro

Columbia University

1989

Air Force Office of Scientific Research

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Approved for public release;
distribution unlimited.

DYNAMICS AND STABILIZATION OF MATERIALS
POSSESSING HIGH ENERGY CONTENT

Prepared by
Nicholas J. Turro

Department of Chemistry
Columbia University
New York, New York 10027

November 1989

Contract: AFOSR-88-0043

Prepared for
Air Force Office of Scientific Research
Building 410
Bolling Air Force Base, D.C. 20332

FINAL REPORT

Dynamics and Stabilization of Materials Possessing High Energy Content

SUMMARY: The accomplished research has involved (1) the construction of new instrumentation for the investigation of transient high energy materials ; (2) the exploration of how the chemistry of transient high energy materials is modified by adsorption on the surfaces at interfaces; and (3) the exploration of how the chemistry and dynamics of high energy density materials respond to systematic variations in structure, and experimental variables such as pressure, magnetic fields and temperature. Particular emphasis has been given to reactions in microheterogeneous environments and interfaces provided by micelles, polymers and porous solids. Since the initiation of this grant, a time resolved resonance Raman spectrometer, a time resolved electron spin resonance spectrometer and a time resolved NMR spectrometer capable of measuring CIDNP (Chemically Induced Dynamic Nuclear Polarization) spectra on a routine basis have been constructed.

High Energy Materials Adsorbed on Porous Solids

The photochemistry of ketones adsorbed on the internal surface of porous solids, such as silica and zeolites, was found to vary dramatically from that observed in homogeneous solution. The basis for the differing behavior has been traced to the control of the diffusional and rotational properties of the intermediate radicals produced by photolysis of the ketones. For example, it was shown that photochemical reactions of ketones adsorbed on zeolite molecular sieves can be controlled dramatically by the number density, charge and size of exchangeable cations associated with the zeolite framework (427, 435, 440, 443). The dramatic influence of site, geometry and size on the diffusion of radicals on zeolite surfaces was demonstrated for the important family of ZSM-5 zeolites (421).

The products could be varied systematically by varying the silicon to aluminum content and the amount of water adsorbed by the zeolite. The role of surfaces in controlling the reactions of high energy species was strikingly demonstrated by the observation that photochlorination of straight chain hydrocarbons adsorbed on ZSM-5 zeolites occurs selectively at the terminal position, whereas photochlorination of same materials in solution results in completely non-selective chlorination at all positions (424). The quenching of triplet state benzophenone adsorbed on porous silica by oxygen has been investigated by time resolved diffuse reflectance laser spectroscopy. Diffusion within the restricted pore geometry of a series of silica was modeled as a target annihilation reaction in three dimensions (425, 426), and a general scaling behavior was found that related the rate of the annihilation to the characteristic mean pore size of the silica. The scaling behavior was found to be that predicted by a simple random walk of the oxygen molecules diffusing within the pore space. The direct observation of benzyl radicals produced by photolysis of dibenzyl ketone adsorbed on porous silica by electron spin resonance was achieved (419). The size of the silica pores and the presence and absence of water were found to influence the observed spectra in a manner consistent with the occurrence of two bound forms of the radicals, on a freely diffusing surface species and the other a more tightly bound surface species. Excited state resonance Raman spectroscopy has been shown to be a sensitive technique to characterize the hemicelles which are formed when surfactants are adsorbed from aqueous solvents onto porous solids (432). Ru(II) complexes were employed as photoluminescence probes which were shown to be sensitive to the solid liquid interface produced by formation of the hemimicelles. Research on photoluminescent metals was extended to ruthenium complexes (437). Dramatic magnetic isotope and magnetic field effects on the product distribution of photolysis of dibenzyl ketone adsorbed on zeolites were discovered (442). An extension of the research on photochemistry of molecules adsorbed on porous solids was made to solid complexes of ketones and aqueous solutions of stilbene and cyclodextrins (444, 446)

Structure and Dynamics of High Energy Reactive Intermediates

A time resolved laser spectroscopic investigation of the interaction of triplet enones with ethylenes has provided kinetic evidence for the mechanism of this important class of photoreactions (431). The pressure dependence of the mechanism of the cycloaddition of ethylene to ketones was investigated (429). The first example of hyperconjugation in directing the selectivity of photoreactions was discovered (430). An investigation of the photochemistry of benzocyclobutene was shown to yield isomeric products that result from a rearrangement of a photochemically produced high energy benzene isomer to a carbene (423). These results provide insight into the role of energy surfaces in interconverting species of enormous energy content. The influence of molecular geometry on the spectroscopic and photochemical properties of a series of benzophenone cyclophanes was investigated (441). A novel method for the investigation of electron spin transfer through spin polarization transfer to a stable nitroxide was invented (447). The first investigation of the pressure induced variation in the diastereoselectivity in photoinduced Diels-Alder reactions was reported (448).

Radicals and Biradicals

Nanosecond transient absorption studies of the lifetimes of several substituted biradicals elucidated the mechanisms which determine the lifetime of these reactive intermediates (422, 436, 438, 439). It was established that spin-orbit coupling provides the major mechanism for intersystem crossing when the biradical possesses an acyl radical center and that nuclear-electron hyperfine coupling provide the mechanism for intersystem crossing when a hydrocarbon biradical is generated. The lifetime of a hydrocarbon biradical was found to depend on the presence of lanthanide (III) ions. No net reaction occurred. It was proposed that an electron spin exchange between the biradicals is responsible for the quenching of the biradical. These results demonstrate the ability to manipulate

the lifetimes of high energy species by inert quenchers whose structures and efficiencies of quenching can be varied. The importance of the size of the hyperfine constant in determining CIDNP effects was determined (445).

Polymers

A review of the use of photoluminescence and spin methods as probes of polymer interfaces and structures was published (417). Examples from AFOSR supported research on the binding, conformation and association of water soluble polymers were emphasized.

II. Coupling Activities

In July 1989 Dr. Don Ball visited our laboratories and was involved in detailed discussions of our current research activities. At the V International Symposium on Inclusion Phenomena and Molecular Recognition in September 1988 in Orange Beach, Alabama, the principal investigator and Dr. Larry Burggraf were involved in several extended discussions concerning the use of photochemical methods to attack problems in interface science. The possible use of Dr. Burggraf's novel method of using specifically shaped holes to control photochemical processes was explored.

The Principal Investigator was presented with a major award during 1988: The James Flack Norris Award in Physical Organic Chemistry of the Northeastern Section of the American Chemical Society. He was the "Frontiers in Chemical Research Lecturer" at Texas A&M University (May 1988) and presented a series of lectures at the Royal Institute of Technology in Stockholm (May 1988) and presented a lecture at a workshop on Photochemistry of Polymers sponsored by the European Polymer Federation in Stockholm. He also presented lectures at Caltech, UCLA, Berkeley, University of California at Fullerton, New York University, University of

Washington, University of Victoria (Canada) and University of British Columbia (Canada), Rohm and Haas, Ciba-Geigy and E. I. DuPont. He presented papers at the Gordon Research Conference on Physical-Organic Chemistry, the Gordon Research Conference on Organic Photochemistry, the Inter-American Photochemical Society, the American Chemical Society in Miami Beach (Polymer Division and Physical Chemistry Division)

The Principal Investigator is the co-Chairman of the National Academy of Sciences Board on Chemical Sciences and Technology, and he serves on an Advisory Committee to the Chemistry Division of the Office of Naval Research and on the Science Advisory Committee of the Council for Chemical Research. He also serves on the Advisory Boards of the **Journal of the American Chemical Society**, the **Journal of Photochemistry**, the **Journal of Reactive Intermediates**, **Langmuir**, and the **Encyclopedia of Physical Science and Technology**.

References

417. N.J. Turro, "Photons and Spins in the Service of Polymer Science: Luminescence, Photochemical, NMR and ESR Probes of Polymer Interfaces and Surfaces," **Polymer Preprints**, 29, 500 (1988).
419. N.J. Turro, K.C. Waterman, K.M. Welsh, M.A. Paczkowski, M.B. Zimmt and C.C. Cheng, "Use of Electron Spin Resonance Spectroscopy to Study Photochemistry of Adsorbed Dibenzyl Ketone on Porous Silica," **Langmuir**, 4, 677 (1988).
421. L. Abrams, D.R. Corbin, and N.J. Turro, "Size, Shape and Site Selectivities in the Photochemical Reactions of Molecules Adsorbed on Pentasil Zeolites," **Characterization of Porous Solids**, K.K. Unger *et al.*, (Eds.), Elsevier Science Publishers B.V., Amsterdam, 1988.
422. J.F. Wang, K. M. Welsh, K.C. Waterman, P. Fehlner, C.E. Doubleday, Jr., and N.J. Turro, "Dynamics of Interaction

- between a 1,9-Biradical and Lanthanide Ions," **J. Phys. Chem.**, **92**, 3730 (1988).
423. N. J. Turro, Z. Zhang, W.S. Trahanovsky, and C. -H. Chou "Photochemistry of Benzocyclobutene," **Tetrahedron Letters**, **29**, 2543-2546, (1988)
424. N.J. Turro, J.R. Fehlner, D.P. Hessler, K.M. Welsh, W. Ruderman, D. Firnberg, and A.M. Braun, "Photochlorination of n-Alkanes Adsorbed on Pentasil Zeolites," **J. Org. Chem.**, **53**, 3731 (1988).
425. J.M. Drake, P. Levitz, N.J. Turro, K.S. Nitsche, "Benzophenone Triplet Quenching by Oxygen at the Gas/Solid Interface: A Target Annihilation Reaction in the Restricted Pore Geometry of Silica," **J. Phys. Chem.**, **92**, 4680 (1988).
426. J.M. Drake, P. Levitz, J. Klafter, N.J. Turro, K.S. Nitsche and K.F. Cassidy, "Gas Phase Quenching of Excitations as a Probe of Dynamics in Porous Silicas," **Phys. Rev. Letts.**, **61**, 865 (1988).
427. N.J. Turro, "Photochemical Probes for the Structure of Zeolites and for Dynamics of Reactions of Molecules Adsorbed on Porous Solids," in **Ultrastructure Processing of Advanced Ceramics**, ed., by J.D. MacKenzie and D.R. Ulrich, John Wiley & Sons, New York: 1988, pp. 603-612.
429. N.J. Turro, W.-S. Chung and M. Okamoto, "Pressure Effects on the Photocycloaddition of 2-Adamantanone with Fumaronitrile," **J. Photochem. and Photobiol., A: Chemistry**, **45**, 17 (1988).
430. W.-S. Chung, N.J. Turro, S. Srivastava, H. Li and W.J. le Noble, "Hyperconjugation as a Factor in Face Selectivity during Cycloaddition," **J. Am. Chem. Soc.**, **110**, 7882 (1988).
431. D.I. Schuster, G.E. Heibel, P.B. Brown, N.J. Turro and C.V. Kumar, "Are Triplet Exciplexes Involved in [2+2]

Photocycloaddition of Cyclic Enones to Alkenes?" *J. Am. Chem. Soc.*, *110*, 8261 (1988).

432. P. Somasundaran, J.T. Kunjappu, C.V. Kumar, N.J. Turro and J.K. Barton, "Excited State Resonance Raman Spectroscopy as a Probe of Alumina-Sodium Dodecyl Sulfate Hemimicelles," *Langmuir*, *5*, 215, 1989.
435. N.J. Turro, "Photochemical Probes for Structure of Zeolites and for Dynamics of Reactions of Molecules Adsorbed on Porous Solids," in *Molecular Dynamics in Restricted Geometries*, ed. J. Klafter and J.M. Drake, John Wiley & Sons, Inc. 1989, pp. 387-404.
436. J.F. Wang, C. Doubleday, Jr., and N.J. Turro, "Negative Temperature Dependence in the Decay of Triplet Biradicals," *J. Am. Chem. Soc.*, *111*, 3962 (1989).
437. H. Holden Thorp, C.V. Kumar, N.J. Turro and H.B. Gray, "Emission Properties of Dioxorhenium(V) Complexes in Aqueous Solutions of Anionic and Nonionic Surfactants: A Sensitive Probe of Hydrophobic Binding Regions," *J. Am. Chem. Soc.*, *111*, 4364 (1989).
438. C. Doubleday, Jr., N.J. Turro and J.F. Wang, "Dynamics of Flexible Triplet Biradicals," *Acc. Chem. Res.*, *22*, 199 (1989).
439. J.F. Wang, C. Doubleday, Jr., and N.J. Turro, "Large Magnetic Field Effect on the Decay Rates of Triplet Hydrocarbon Diradicals," *J. Phys. Chem.*, *93*, 4780 (1989).
440. N.J. Turro and Z. Zhang, "Photochemistry of Dibenzyl Ketone Adsorbed on Size/Shape Selective Faujasite Zeolites. Steric Effects on Product Distributions," in *Photochemistry on Solid Surfaces*, ed. M. Anpo and T. Matsuura, Elsevier, New York 1989.
441. N.J. Turro, I.R. Gould, J. Liu, W.S. Jenks, H. Staab and R. Alt, "Investigations of the Influence of Molecular Geometry on the Spectroscopic and Photochemical Properties of α -Oxo[1.*n*]paracyclophanes (Cyclophanobenzophenones)," *J. Am. Chem. Soc.*, *111*, 6378 (1989).

442. N.J. Turro and Z. Zhang, "Magnetic Isotope and Magnetic Field Effects on the Product Distributions of Photolyses of Dibenzyl Ketone Adsorbed on Zeolites," **Tetrahedron Letters**, *30*, 3761 (1989).
443. N.J. Turro, "Dynamics of Radical Pairs and Biradicals Adsorbed on Zeolites," **Polymer Preprints**, 565 (1989).
444. V. Pushkara Rao and N.J. Turro, "Asymmetric Induction in Benzoin by Photolysis of Benzaldehyde Adsorbed in Cyclodextrin Cavities," **Tetrahedron Letters**, *30*, 4641 (1989).
445. H.D. Roth, R.S. Hutton, K.C. Hwang, N.J. Turro and K.M. Welsh, "Chemically Induced Dynamic Nuclear Polarization in Systems Containing Large Hyperfine Coupling Constants," **J. Phys. Chem.**, *93*, 5697 (1989).
446. G.L. Duveneck, E.V. Sitzmann, K.B. Eisenthal, and N.J. Turro, "Picosecond Laser Studies on Photochemical Reactions in Restricted Environments: The Photoisomerization of *trans*-Stilbene Complexed to Cyclodextrins," **J. Phys. Chem.**, *93*, 7166 (1989).
447. W.S. Jenks and N.J. Turro, "Indirect Observation of Spin Polarization in Triplet Fluorenylidene at Room Temperature," **Tetrahedron Letters**, *30*, 4469 (1989).
448. W.S. Chung, N.J. Turro, J. Mertes and J. Mattay, "Pressure-Induced Diastereoselectivity in Photoinduced Diels-Alder Reactions," **J. Org. Chem.**, *54*, 4881 (1989).

Nicholas J. Turro November 6, 1989

papers submitted or in press

1. W.S. Chung, N.J. Turro, J. Silver and W.J. le Noble, "Modification of Face Selectivity by Inclusion in Cyclodextrins," **J. Am. Chem. Soc.**, in press.
2. J.F. Wang, V.P. Rao, C. Doubleday, Jr., and N.J. Turro, "Combined Effect of Isotopic Substitution, Temperature, and Magnetic Field on the Lifetimes of Triplet Biradicals," **J. Phys. Chem.**, in press.
3. R.A. Moss and N.J. Turro, "Laser Flash Photolytic Studies of Arylhalocarbenes," in **Kinetics and Spectroscopy of Carbenes and Biradicals**, ed. M. Platz, Plenum Publishing Corp, New York, in press.
4. G. Orellana, A. Kirsch-De Mesmaeker and N.J. Turro, "⁹⁹Ru NMR of Ruthenium(II) Polypyridyl Complexes," **Inorganic Chemistry**, in press.
5. M.C. Moreno-Bondi, G. Orellana and N.J. Turro, "Photoinduced Electron Transfer Reactions to Probe the Structure of Starburst Dendrimers," **Macromolecules**, in press.
6. V.P. Rao, J.F. Wang, N.J. Turro and C. Doubleday, Jr., "Synthesis of ¹³C and 2H-Labelled 2-Phenylcyclododecanones," **J. Labelled Compounds and Radiopharmaceuticals**, in press.
7. V.P. Rao, N. Han and N.J. Turro, "A Fine-Tuning of Photoreactivity of Large Ring 2-Phenylcycloalkanones Adsorbed in Cyclodextrins," **Tetrahedron Letters**, submitted.
8. V. Ramamurthy, D.R. Corbin, C.V. Kumar and N.J. Turro, "Modification of Photochemical Reactivity by Zeolites: Cation Controlled Photodimerization of Acenaphthylene within Faujasites," **Tetrahedron Letters**, in press.
9. V. Ramamurthy, D.R. Corbin, D.F. Eaton and N.J. Turro, "Modification of Photochemical Reactivity by Zeolites; Role of Cations in Controlling the Behavior of Radicals Generated within Faujasites," **Tetrahedron Letters**, in press.
10. V. Ramamurthy, D.R. Corbin, N.J. Turro and Y. Sato, "Modification of Photochemical Reactivity by Zeolites: Cation Enhanced α -Cleavage of Aryl Alkyl Ketones Included in Faujasites," **Tetrahedron Letters**, in press.
11. C. Malbrel, P. Somasundaran and N.J. Turro, "In-Situ Kinetics Measurements of Surfactant Adsorption on Colloidal Alumina Using ESR Spectroscopy," **J. Colloid & Interface Science**, in press.
12. N.J. Turro, "Photochemistry of Organic Molecules Adsorbed on Faujasite Zeolites. Steric Effects on Product Distributions," in **Inclusion Phenomena and Molecular Recognition**, Plenum Publishing Corp., in press.

13. N.J. Turro, "Physical Organic Photochemistry," **J. Photochem. & Photobiol.**, in press.
14. M. Garcia-Garibay and N.J. Turro, "Topological Connectivity Between Organized Assemblies", in **Photochemistry in Organized and Constrained Media**, VCH Publishers, New York, in preparation.

Participating Professionals

Collaborators:

1. Dr. Lloyd Abrams, E.I. duPont de Nemours, Wilmington, DE 19898
2. Dr. David Corbin, E.I. duPont de Nemours, Wilmington, DE 19898
3. Dr. V. Ramamurthy, E.I. duPont de Nemours, Wilmington, DE 19898
4. Professor Kenneth B. Eisenthal, Department of Chemistry, Columbia University, New York, NY 10027
5. Professor Walter Trahanovsky, Department of Chemistry, Iowa State University, Ames, Iowa
6. Professor James R. Fehner, Department of Chemistry, Pennsylvania State University, Worthington Scranton Campus, Dunmore, PA 18512
7. Dr. W. Ruderman, INRAD Corporation, Northvale, NJ 07647
8. Dr. Andre M. Braun, Institute de Chimie Physique, Ecole Polytechnique Federale de Lausanne, Lausanne, SWITZERLAND
9. Dr. J. Michael Drake, Exxon Corporation, Annandale, NJ 08801
10. Dr. Pierre Levitz, Exxon Corporation, Annandale, NJ 08801
11. Dr. Joseph Klafter, Exxon Corporation, Annandale, NJ 08801
12. Professor William J. le Noble, Department of Chemistry, SUNY Stony Brook, New York 11794
13. Professor David I. Schuster, Department of Chemistry, New York University, New York, NY 10003

14. Professor P. Somasundaran, Langmuir Center for Colloids & Interfaces, Columbia University, NY, NY 10027
15. Professor Harry B. Gray, Division of Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, CA 91125
16. Professor Heinz Staab, Abteilung Organische Chemie, Max-Planck-Institute für Medizinische Forschung, D-6900 Heidelberg, FRG.
17. Dr. Heinz D. Roth, AT&T Bell Laboratories, Murray Hill, NJ 07974.
18. Professor Jochen Mattay, Institut für Organische Chemie der RWTH-Aachen, 5100 Aachen, FRG.
19. Professor Robert A. Moss, Department of Chemistry, Rutgers, the State University of New Jersey, New Brunswick, NJ
20. Professor Andree Kirsch-De Mesmaeker, Service de Chimie Organique, Université Libre de Bruxelles, Brussels, Belgium

Advanced Degree Awarded

Zhenyu Zhang, Ph.D. Columbia University, October 1989.

Thesis title: I. Photochemistry of Dibenzyl Ketone and Its Derivatives Adsorbed on Size/Shape Selective Zeolites. II. Photochemistry of Benzocyclobutene